

THE COMPOSITION OF HEAVY MOLECULAR IONS
INSIDE THE IONOPAUSE OF COMET HALLEY

D.L. Mitchell, R.P. Lin, K.A. Anderson, C.W. Carlson, D.W. Curtis
Space Sciences Laboratory, University of California, Berkeley, CA U.S.A.

A. Korth
Max-Planck-Institut für Aeronomie, Lindau, F.R.G.

H. Rème, J.A. Sauvaud, C. d'Uston
Centre d'Etude Spatiale des Rayonnements, CNRS, Toulouse, France

D.A. Mendis
Department of Electrical Engineering and Computer Sciences
University of California, San Diego, CA U.S.A.

The RPA2-PICCA instrument aboard the Giotto spacecraft obtained 10–210 amu mass spectra of cold thermal molecular ions in the coma of Comet Halley. Outside the ionopause ($r > 4700$ km), the thermal energy spread of the ions limits the effective mass resolution of PICCA to about 3 amu. However, several important features of the mass spectrum are observed at this resolution (Mitchell *et al.*, 1987). Above 50 amu, there is an ordered series of mass peaks composed of three or more closely spaced masses and centered at 61, 75, 90, and 105 amu. The separations of the peak centers are characteristic of molecules rich in carbon, hydrogen, oxygen, and nitrogen. The peak abundances decrease smoothly with increasing mass. The average loss rate of 55–69 amu ions is roughly 10^{-4} per second, or four times the H_2O loss rate, which results from the photodissociation of a single H-O bond. The loss rate increases with mass to about 5.5×10^{-4} per second for 98–114 amu ions. This suggests that the heavy molecules are predominantly singly bonded, and that the number of single bonds per molecule increases with mass.

Inside the ionopause the ion temperature drops to $kT = 0.03$ eV, allowing optimal mass resolution ($\lesssim 1$ amu). High resolution data were obtained from 35 to 70 amu, revealing the dominant masses at 43, 45, 47, 48, 57, 59, 61, and 63 amu. The mass composition derived from the high resolution spectra is consistent with lower resolution spectra taken just outside the ionopause, which shows that there is no abrupt change in composition across the ionopause.

The dissociation products of the long chain formaldehyde polymer polyoxymethylene (POM) have recently been proposed as the dominant complex molecules in the coma of Comet Halley (Heubner, 1987); however, POM alone cannot account for all of the features of the high resolution spectrum. The dominant masses between 55 and 70 amu are separated by 2 amu; therefore the peak width must result from variations in the C:O ratio and not from the dissociation and attachment of hydrogen atoms. The observed 63 amu molecule, for example, can be produced by replacing an H on the

methylene unit of HOCH₂O with an OH, which gives the oxygen-rich molecule HOCHOHO. However, a relatively abundant 57 amu molecule cannot be produced in a similar manner without eliminating the oxygen altogether and is thus likely to result from a species unrelated to POM.

An important component of the dust at Comet Halley is particles highly enriched in carbon, hydrogen, oxygen, and nitrogen relative to the composition of carbonaceous chondrites (Clark *et al.*, 1987). Since this dust could be a source for the heavy molecules observed by PICCA, we began the search for other chemical species by determining all the molecules with mass between 20 and 120 amu which can be made from the relatively abundant C, H, O, and N, without regard to chemical structure. The only criterion for a valid molecule was that it have enough chemical bonds to hold itself together. The total number of possible CHON molecules as a function of mass shows peaks which agree quite well with the locations of the observed mass peaks in the PICCA data.

The composition of interstellar grains could be relevant to comets if the latter consist of essentially unmodified interstellar material. Laboratory experiments designed to simulate the chemical processes that take place on interstellar dust grains during the formation and evolution of icy mantles have recently been performed (Shutte, 1988). First, a gas mixture of H₂O, CO, NH₃, and CH₄ was deposited onto a 12° K aluminum "grain surface" under simultaneous ultraviolet irradiation. The UV radiation created radicals which could either react or be stored within the cold icy substrate. Subsequent warm-up of the icy mantle allowed first the radicals and then the non-radicals to diffuse and react, producing progressively more complex molecules. After warm-up to room temperature, there remained on the grain surface a refractory organic residue, which was composed of molecules which cluster near the mass peak locations observed by PICCA. Most of these molecules appear to be made up of molecular units (CH₂, NH₂, OH, and CO) connected by single bonds.

Molecules which are constructed from CH₂, NH, O, and H units connected by single bonds can produce a spectrum that closely resembles the observed high resolution spectra if the nitrogen abundance is less than about 12% (which is consistent with the CHON dust composition, Langevin *et al.*, 1987) and the C/O ratio is 1.2 to 1.4. The 2 amu alternation results since the molecules are constructed mainly from even-mass units. In order for the alternation to fall on odd masses, most molecules must have suffered a single dissociation, leaving only one open bond. This is consistent with the 55-69 amu molecules having traveled only a short distance inside the ionopause (~4000 km) relative to their observed dissociation scale length of 9300 km.

References

- Clark, B.C., L.W. Mason, and J. Kissel, *Astron. Astrophys.*, **187**, 779 (1987).
 Heubner, W.F., *Science*, **237**, 628 (1987).
 Langevin, Y., J. Kissel, J-L. Bertaux, and E. Chassefière, *Astron. Astrophys.*, **187**, 761 (1987).
 Mitchell, D.L., R.P. Lin, K.A. Anderson, C.W. Carlson, D.W. Curtis, A. Korth, H. Rème, J.A. Sauvaud, C. d'Uston, and D.A. Mendis, *Science*, **237**, 626 (1987).
 Shutte, W.A., Ph.D. Thesis, University of Leiden, The Netherlands (1988).